Hydrocracking of Coconut Oil into Gasoline Fraction using NI/Modified Natural Zeolite Catalyst

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Abstract : Hydrocracking reaction of coconut oil into gasoline fraction has been done using mesoporous Ni/modified natural zeolite catalyst with various temperatures. The Ni/modified natural zeolite catalyst was synthesized by destructiing the natural zeolite with 9M HCl solution, then NaOH pellet (NaOH/zeolite ratio = 1.2), followed by treating with 6M NaOH solution, $AlCl_3$, CTAB and distilled water. The mixture was regulated to pH of 11.5. The mixture was then poured into a reactor for hydrothermal process at 150 ^{o}C for 24 h. The synthesized zeolite was characterized using Fourier Transform Infra Red, X-Ray Diffraction, surface area analyzer and Scanning Electron Microscopy. The synthesized zeolite was impregnated by $Ni(Cl)_2.6H_2O$ solution as a precussor produced the Ni/modified natural zeolite sample. The hydrocracking process was carried out in the variation of temperatures of 360, 415, 450 and 500 ^{o}C. The liquid product was analyzed using Gas Chromatography Mass Spectrometer.

The resulted showed that the modified natural zeolite had surface area of 270.628 m^2/g, pore volume of 0.339 cm^3/g, and pore diameter of 9.17 nm. The Ni/modified natural zeolite sample showed the nickel content of 3.5 wt %, Lewis acid sites of 0.0072 mmol/g, Brönsted acid sites of 0.0096 mmol/g, surface area of 88.012 m^2/g, pore volume of 0.153 cm^3/g and pore diameter of 6.972 nm. The hydrocracking of coconut oil indicated that the highest conversion of gasoline fraction was 11.73 wt % obtained at 450 ^{o}C in the liquid product of 31.62 wt %.

Keywords : zeolite, coconut oil, hydrocracking, temperature, gasoline.

Introduction

Catalyst is generally defined as material that can accelerate chemical reaction into product. Transition metal commonly used in catalytic reactions. Support is used to provide greater surface area for the transition metals as the active phase. Zeolite is porous solid composed of silica and alumina framework that can be used as support. Type of zeolite is based on the formation process consisting of synthetic zeolite and natural zeolite. Natural zeolite generally found in mixture with other type of zeolite and amorphous mineral such as feldspar, silica, clay, transition metal oxide, and organic contaminants[1]. Natural zeolite can not be directly used as a catalyst or support catalyst due to non-zeolite material content is high. So far it has made efforts to acquire natural zeolite with a high purity zeolite and can be used as a catalyst or metal catalyst support[2-4]. But such researchs had not produced natural zeolite with a high purity. Natural zeolite has silica content (SiO_2) and alumina (Al_2O_3) that is still fused and chemically bonded in thenatural zeolite. The treatment of the natural

zeolite include destruction using HCl at high concentration and fusion with NaOH pellet to obtain free of silica and alumina as the raw material for the synthesis of zeolite[5-7]. Silica and alumina free obtained from fusion of natural zeolite can be used for synthesis of zeolite. Pore size of zeolite is generally microporous that will limit its application in catalytic conversion of a hydrocarbon with a large molecule such as petroleum oil, triglycerides to be short chain hydrocarbon fraction. Mesoporou zeolite material has been synthesized and introduced by previous researchers[8-11]. Synthesis of mesoporous zeolite with the addition of NaOH solution had been conducted and reported that the addition of NaOH solution to produce zeolite mesoporous size is not too large, but a large pore size obtained after the addition of NaOH and followed by formation in hydrothermal reaction[12]. Synthesis of mesoporous zeolite by adding NaOH solution whose concentration was vary and surfactant (CTAB) that concentration was kept as well as followed by formation in hydrothermal reaction. The result showed that NaOH, CTAB and hydrothermal process increase the surface area and pore size significantly[13]. Several researches have been conducted about the cracking of palm oil as source of hydrocarbons. Palm oil was pre-treated to produce methyl ester of palm oil as feedstock in the catalytic cracking reaction in a flow-fixed bed reactor system and Ni/natural zeolite catalyst was used to produced gasoline fraction of 18.35% at 500 ^{o}C[14]. Conversion palm oil using Cr/natural zeolite into liquid products was 82.05% resulted from the ratio of the feed/catalyst of 2/1 with the preliminary preparation of the feed through the esterification reaction[15]. Conversion palm oil (crude oil of palm oil as feed) using NiMo/natural zeolite catalyst, the simultaneous cracking and hydrogenation of palm oil was carried out in a liquid phase batch reactor and yield of gasoline fraction was 11.93%[4].

Based on the above presentation, the authors conducted utilization of the modified natural zeolite as a support for nickel metal that was used as a catalyst on the hydrocracking of coconut oil into gasoline fraction. The zeolite was synthesized using silica and alumina from natural zeolite with fusion treatment. The hydrocracking process was carried out at various temperatures of 360, 415, 460 and 500 ^{o}C. Coconut oil hydrocracking at that temperature variations have not been studied.The results were discussed in the following section.

Experimental

Materials

Natural zeolite was obtained from Klaten, Central of Java, Indonesia. The chemicals used were HCl 37%, NaOH pellet, AlCl$_3$, pyridine, pH universal paper, Ni(Cl)$_2$.6H$_2$O) that purchased from E.Merck, and cetyltrimethyl ammonium bromide (Aldrich). N$_2$ gas, O$_2$ gas, H$_2$ gas and aquadest were purchased from Physical Chemistry Lab, Department of Chemistry FMIPA UGM. Coconut oil was purchased from a super market in Yogyakarta.

Instrumentation

Fourier Transform Infra Red (FTIR): Shimadzu Prestige 21, The X-Ray Diffraction (XRD) : Shimadzu-6000 XRD and Scanning Electron Microscopy (SEM) : JEOL JSM-6360LA. Surface area analyzer : NOVA 1200 (QUANTACHROME). Gas Cromatography - Mass Spectrometer (GC-MS): GS-2010 Shimadzu. The hydrocracking reaction was performed in a continuous flow fixed bed reactor.

Procedure

Synthesis of modified natural zeolite and Ni/modified natural zeolite catalyst

Natural Zeolite (NZ) was grinded and sieved (100 mesh). The zeolite (15 g) was destructed using 20 mL of 9M HCl at 100 ^{o}C followed with refluxing mixture for 6 h. The zeolite was filtered and washed using deionized aquadest until neutral condition, dried on the oven at 120 ^{o}C for 3 h. The zeolite was fused with NaOH pellet (NaOH/zeolite ratio = 1.2), then calcined at 500 ^{o}C. The zeolite (8 g) was mixed with 6M NaOH (3.5 mL), AlCl$_3$ (0.8 g) , CTAB (1.2 g) and distilled water was added to adjusted pH 11.5 while stirring for 48 h at room temperature. Then, the zeolite sample was hydrothermally treated at 150 ^{o}C for 24 h. The synthesized zeolite was then washed using aquadest until the solution reached pH of 6, then filtered followed by dried and calcined at 550 ^{o}C for 6 h. The synthesized zeolites was characterized by means of mineral type, surface area, pore volume, and diameter.

The Ni/modified natural zeolite (Ni/MNZ) catalyst was prepared by a wetness impregnation[2,16,17]. The Nickel metal loading was 3.5 wt % based on the weight of zeolite. The $Ni(Cl)_2.6H_2O$ precursor of 0.7085 g was solved into 15 mL of H_2O, then 5 g of modified natural zeolite (MNZ) sample was added. The mixture was then evaporated and dried in an oven at 120 °C for 3 h. The catalyst sample was calcined using N_2 at 550 °C for 3 h, oxidized using O_2 at 500 °C for 2 h, and reduced using H_2 at 500 °C for 2 h. The catalyst was characterized included surface area, pore volume, diameter using surface area analyzer, and the catalyst acidity was determined using pyridine vapour as an adsorbed base then analyzed using FTIR. Amount of Brönsted and Lewis acid sites was calculated based on the Emeis equation[18,19].

Hydrocracking process of coconut oil using Ni/MNZ catalystt

Activity test of Ni/MNZ catalyst was done in continuous flow-fixed bed reactor under reaction condition of oil/catalyst ratio of 50, and H_2 gas flow rate of 25 mL/min. The coconut oil was heated and flowed into the catalyst reactor and heated at various temperature of 360, 415, 450 and 500 °C. Result of hydrocracking was passed in colling system and organic liquid product fraction was collected and analyzed using GC-MS. The conversion was calculated as a following:

$$Liquid\ product\ conversion\ (wt\ \%) = \frac{W2\ (g)}{W1\ (g)} \times 100\%$$

where, W1 = initial feed weight (before hydrocracking process)
W2 = liquid product weight (g)

$$Coke\ (wt\ \%) = \frac{WC2\ (g) - WC1\ (g)}{W1\ (g)} \times 100\%$$

Where, WC1 = catalyst weight before hydrocracking process
WC2 = catalyst weight after hydrocracking process

$$Yield\ (wt\ \%) = \frac{G\ (g)}{W1\ (g)} \times 100\%$$

Where, G = the gasoline-grade hydrocarbons volume in the reactor products
W1 = initial feed weight (before hydrocracking process)
Gas product conversion (wt %) = {100 - (liquid product conversion + coke)} x100%

Results and Discussion

Characteristic of MNZ and Ni/MNZ catalyst

Fig.1a and 1b can be seen FTIR spectra of the NZ and MNZ with characteristics based on the wave number of the zeolite mineral[20,21].
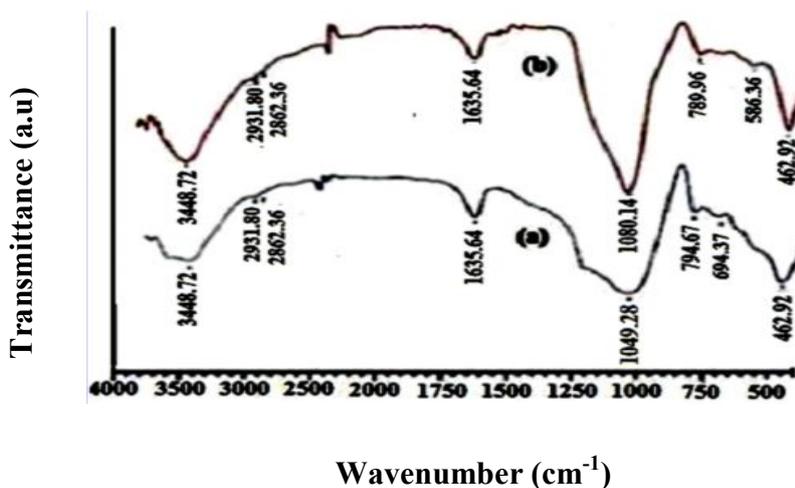

Fig.1. Spectra FTIR of (a) NZ (b) MNZ

Fig.1a for the NZ showed that wave number at 3448.72, 2931.80, 2862.36, 1635.64, 1049.28, 794.67, 694.37, and 462.92 cm^{-1} for Si-OH bonding (silanol), asymmetric stretching vibration of C-H, symmetric stretching vibration of C-H, O-H group bending vibration of the adsorbed water molecules, TO4 (Si-O and Al-O are finger print of zeolite), symmetric stretching vibration of Si-O and Al-O, symmetric stretching vibration of Si-O and Al-O, bending vibration of Si-O and Al-O respectively. Fig.1b showed some peaks of the MNZ that can be stated as follows: At wave number of 3448.72, 2931.80, 2862.36, 1635.64, 1080.14, 789.96, 586.36 cm^{-1} and 462.92 cm^{-1} for Si-OH bonding (silanol), asymmetric stretching vibration of C-H, symmetric stretching vibration of C-H, an O-H group bending vibration of the adsorbed water molecules, TO4 (Si-O and Al-O are finger print of zeolite), symmetric stretching vibration of Si-O and Al-O, double ring, bending vibration of Si-O and Al-O respectively.

From the data in Fig.1a in the wave number of 3448.72 and 1049.28 cm^{-1} were Si-OH bonding (silanol) and the symmetric vibration area of TO4. Whereas from the data in Fig.1b in the wave number of 3448.72 and 1080.14 cm^{-1} were Si-OH bonding (silanol) and the symmetric vibration area of TO4. Between the NZ and MNZ there were differences in sharpness.The NZ before modified seen the peak of the peak was widened. Between the NZ and MNZ there were differences in sharpness.The NZ before modified seen the peak of the peak was widened. On the other hand after the NZ was modified has peaks sharper.This indicates that there has been increasing character of zeolite. The MNZ was more homogeneous compared with that of the NZ.
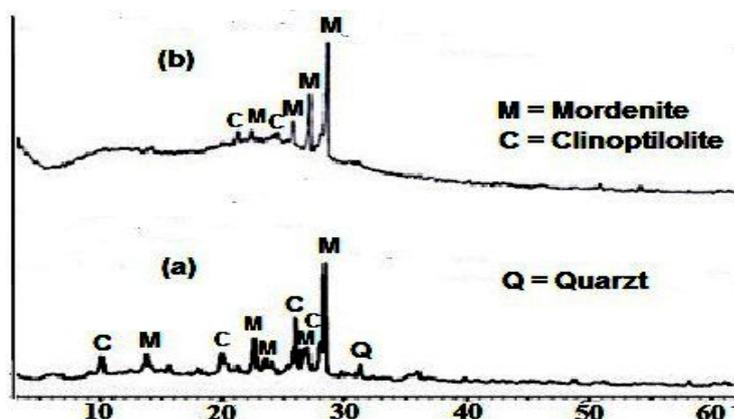

Fig.2. Diffractogram of (a) NZ , (b) MNZ

The XRD results in Fig. 2a showed that the NZ was composed of various minerals which showed heterogeneity implies. Impurities contained in the NZ still higher. The mineral content of NZ from Klaten based on 2Θ include: mordenite , clinoptilolite and quarzt, as well as other amorphous mineral. The dominant mineral content in the NZ based on strong peaks was mordenite based on its 2Θ.

Furthermore, based on 2Θ of the results XRD diffractogram of the MNZ presented in Fig.2b showed that result of modified natural zeolite composed of crystalline peaks were sharper and higher and the highest peak at 2Θ = 27.99, d = 3.18. The minerals contained in the MNZ were mordenite and clinoptilolite. Mordenite was the dominant mineral of the MNZ.

Synthesis of zeolite from raw material that its silica and alumina were still fused and chemically bonded such as natural zeolite, fly ash, volcanic ash generally produced a mixture zeolite[22-25].
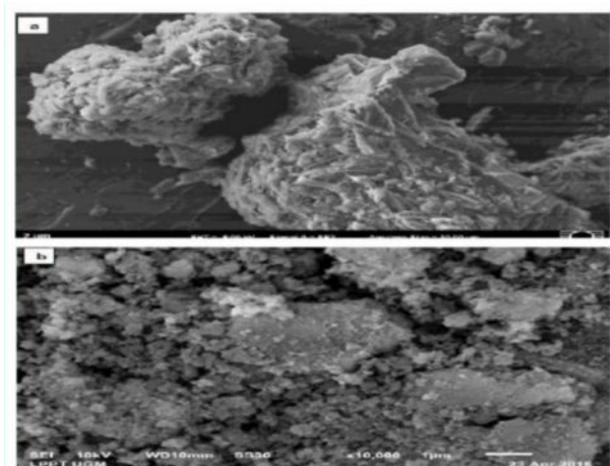
Fig.3. Results of SEM: a) NZ magnification of 10.000x b) MNZ magnification of 10.000x

From the data of SEM presented on Fig.3 can be seen that:

For the NZ (Fig.3a), no crystalline granules and there were impurities in the form of non-zeolite. In Fig. 3b the mineral content of the MNZ was more homogeneous compared with that of the NZ. The results of the determination of surface area, pore volume and diameter of the NZ, MNZ and Ni/MNZ sample presented in Table 1.

Table 1. Characteristics of NZ, MNZ, and Ni/MNZ sample

Shape of zeolite	Lewis acid sites (mmol/g)	Brönsted acid sites (mmol/g)	Total acidity (mmol/g)	Surface area (m^2/g)	Pore Volume (cm^3/g)	Pore diameter (nm)
NZ	-	-	-	17.222	0.082	3.978
MNZ	-	-	-	270.628	0.339	9.17
Ni/MNZ	0.0072	0.0096	0.0168	88.012	0.153	6.972

The surface area, pore volume and diameter of the NZ were smaller than that of the MNZ. This condition may be becaused by the organic impurities and other non-zeolite material that covered the surface and pore of the NZ. The MNZ sample showed average pore diameter of 9.17 nm that was classified as a mesopore. Furtheremore, the MNZ sample after impregnation with nickel metal formed Ni/MNZ sample showed surface area, pore volume and diameter   that were decreased from the value before the impregnation. The decrease may be due to the coverage of big portion of pores by nickel impregnation. However, the pore diameter of Ni/MNZ sample was still in the mesoporous range. Base on the Emeis equation[18,19] and IR data it can be found that the acidity of Ni / MNZ sample was Lewis and Brönsted acid sites of 0.0072 mmol / g and   0.0096 mmol / g.

Result of hydrocracking catalytic reaction of coconut oil to be short chain fraction using Ni/MNZ catalyst

Table 2 showed results of coconut oil hydrocracking using Ni/MNZ catalyst with various of temperatures.

Table 2. Hydrocracking results of coconut oil using Ni/MNZ catalyst

Temperature of catalyst (^{o}C)	Conversion of liquid organic product (wt %)	Conversion of gas fraction(wt %)	Conversion of coke (wt %)
360	35.880	63.840	0.280
415	33.480	66.200	0.320
450	31.620	68.110	0.270
500	31.610	68.100	0.029

Base on data in table 2,it was shown that temperature of hydrocracking produced less liquid organic fraction compared with that of the gas fraction. At the temperature of 450 °C, the liquid organic product, the gas fraction and coke were 31.620, 68.110 and 0.270 wt % . In Fig. 4 showed results of hydrocracking of coconut oil using Ni/MNZ catalyst in various of temperatures.
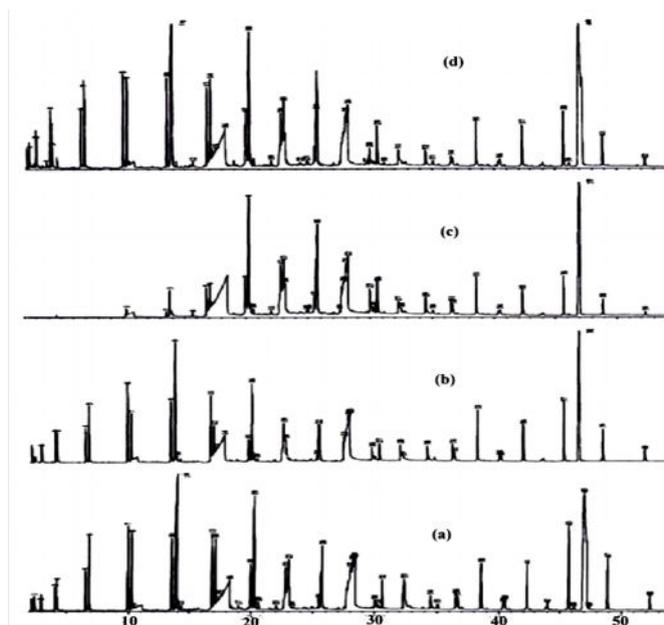

Fig. 4. GC-MS Chromatogram of hydrocracking product of coconut oil using Ni/MNZ catalyst

Base on data in Fig.4 showed that liquid organic fraction resulted in various of compounds. The results of GC-MS for liquid organic product can be expressed as followed:

Fig.4a for the Ni/MNZ catalyst showed that hydrocracking at temperature of 360 °C resulted in carboxylate acid, alkane, alkene, cycloalkane, ketone, alcohol and aromatic were 11.10, 23.26, 17.80, 0.14,11.20,6.30 and 17.17% respectively. Fig.4b, hydrocracking at temperature of 415 °C resulted in carboxylate acid, alkane, alkene, ketone, alcohol, and aromatic were 17.7, 19.88, 24.70, 16.61, 10.86 and 12.02% respectively. Fig.4c, hydrocracking at temperature of 450 °C resulted in carboxylate acid, aldehyde, alkane, alkene, cycloalkane, ketone, alcohol and aromatic were 11.06, 0.34, 30.4, 20.82, 0.86, 10.99, 5.86 and 20.05% respectively. Fig.4d, hydrocracking at temperature of 500 °C resulted in carboxylate, aldehyde (5.45%), alkane, alkene, cycloalkane, ketone, alcohol and aromatic were 14.72, 5.45, 28.49, 17.66, 0.44, 7.83, 2.27 and 19.40% respectively. Cracking reaction of triglyceride will involve disconnection, hydrogenation, isomerization, cyclization and deoxygenation[26]. Cracking a triglyceride will result in shorter carbon chain compound such as carboxylate acid (monoglyceride), alkane, alkene, cycloalkane and aromatic that is result of fat acid forming, hydrogenation, decarboxylation, decarbonylation and hydrodeoxygenation[27].

Hydrocracking of coconut oil to be short chain fraction with various temperatures resulted in alkane compound as main fuel fraction. The hydrocracking process of coconut oil, the greatest alkane content was obtained at 450 °C as presented in Fig.5.
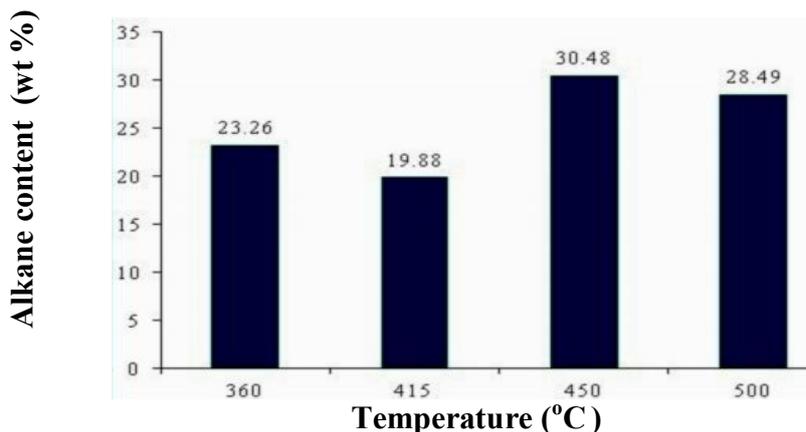
Fig.5. Graph of results on hydrocracking of coconut oil into alkane using Ni/MNZ catalyst

Furthermore, the results of GC-MS of organic liquid product grouped base on the gas fraction, gasoline fraction, diesel fraction and heavy fraction that are presented in Table 3.

Table 3. Product distribution of coconut oil using Ni/MNZ catalyst

Temperature of hydrocracking (^{o}C)	Product distribution (wt %)			
	$< C_7$ (Gas)	$C_7 - C_{12}$ (Gasoline fraction)	$C_{13} - C_{18}$ (Diesel fraction)	$> C18$ (Heavy fraction)
360	63.840	7.36	9.15	19.38
415	66.200	7.78	4.08	21.62
450	68.110	11.73	4.82	15.07
500	68.100	7.41	5.22	18.99

Base on data in table 3, it was shown that temperature of hydrocracking produced various results of the gas fraction, gasoline fraction, diesel fraction and heavy fraction. By rising temperature of hydrocracking, product of gasoline fraction increased as well. However, in this research, at temperature of 450 ^{o}C the highest conversion to be gasoline fraction has reached maximally content. At temperature of 500 ^{o}C, gasoline fraction content decreased back. Decreased in $C_7 - C_{12}$ fraction content may be due to at temperature of 500 ^{o}C , the hydrocracking of coconut oil to be $C_7 - C_{12}$ fraction was lower in liquid organic product. It can be caused, At temperature of 500 ° C may be occured thermal cracking into smaller fraction than C7, so that in liquid organic product decreased too, or cracking of triglycerides into gas fraction was high. It was also appropriate with previous research conducted about cracking of palm oil using zeolite catalyst and obtained a maximum conversion into gasoline fraction at temperature of 450 ^{o}C[28-30]. For diesel fraction and heavy faction, by rising temperature, product of the diesel fraction and heavy fraction ($> C18$) tends to be decreased. The highest conversion of coconut oil to be diesel fraction was 9.15 wt % at temperature of 360 ^{o}C. Whereas for the heavy fraction, the higest conversion of coconut oil to be heavy fraction was 21.62 wt % at temperature of 415 ^{o}C.

Conclusion

The MNZ resulted in mesoporous zeolite mineral crystal. After impregnated to be 3.5 wt % nickel content, the surface area, pore volume and pore diameter decreased but the diameter was still mesoporous range. Liquid organic product after analyzed using GC-MS indicated that the hydrocracking of coconut oil using Ni/MNZ catalyst involved disconnection (cracking) of C – C bonding , hydrogenation, isomerization,

cyclization and deoxygenation. Distribution of yield was various based on catalytic reaction with various of temperatures. The highest conversion of coconut oil to be gasoline fraction ($C_7 - C_{12}$) was 11.73 wt % that obtained at temperature of 450 ^{o}C with 31.620 wt % content in liquid organic product.

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